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<b>(54) Title:</b> INK JET RECORDING SHEET  <b>(57) Abstract</b>  An ink jet recording sheet comprises a support carrying an ink-receiving layer, this layer comprising either (a) a mixture of a derivatized (preferably acetoacetylated) poly(vinyl alcohol) and a non-derivatized poly(vinyl alcohol); or (b) a mixture of a hydrophilic polymer and a poly(vinylbenzyl quaternary ammonium salt) or a poly(vinylpyridine).		

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## INK JET RECORDING SHEET

This invention relates to an ink jet recording sheet which is intended to be printed by an ink jet printer.

Ink jet printers, that is to say printers which form an image by firing a plurality of discrete drops of ink from one or more nozzles on to the surface of a recording sheet placed adjacent the nozzles, have recently enjoyed a large increase in sales. Such ink jet printers have the advantage that they can reproduce good quality text and images, in both monochrome and full color, can produce both reflection prints and transparencies, and are relatively inexpensive to manufacture and to operate, as compared with, for example, color laser printers, thermal wax transfer printers and dye sublimation printers. Accordingly, ink jet printers now dominate the home/small office market, and are often also used to provide color capability not available from the monochrome laser printers typically employed in larger offices.

Although modern ink jet printers can print on almost any conventional paper or similar medium, and indeed are routinely used with commercial photocopying paper for printing text, the quality of images produced by such printers is greatly affected by the properties of the medium used. To produce high quality images reliably, it is necessary that the medium (ink jet recording sheet) used rapidly absorb the ink, in order that the ink does not remain wet for an extended period, since otherwise the ink is likely to smear when successive sheets are stacked in the output tray of the printer. On the other hand, the medium should not promote excessive spreading of the ink droplet, since such spreading reduces image resolution and may result in color distortion if adjacent ink droplets intermix. The medium also should not promote "wicking", that is to say spreading of ink by capillary action through fibrous media, such as paper. The medium must be capable of absorbing the ink without substantial distortion of the medium, since otherwise unsightly "cockling" (formation of ripples and similar folds) may occur, and most observers find such distortions unacceptable. Once the ink has dried, the medium should be such that contact of the image with moist surfaces (such as sweaty fingers)

does not result in bleeding of ink from the image. Finally, since the surface characteristics, such as smoothness, glossiness and feel, of the image are largely determined by the same characteristics of the medium, the medium should possess characteristics appropriate to the type of image being printed. When, as is  
5 increasingly common, an ink jet printer is used to print a digital image produced by a camera or a scanner, the medium should be smooth and possess the high gloss and smooth feel of conventional silver-halide based photographic printing paper.

It is difficult to reconcile all these demands upon an ink jet printing medium and, as shown by the literature, much research has been dedicated to  
10 improving such media. For example, US-A-4 592 951 describes an ink jet recording sheet comprising a transparent support carrying a layer of cross-linked poly(vinyl alcohol). US-A-4 575 465 describes an ink jet recording sheet comprising a transparent support carrying a layer formed from a mixture of vinylpyridine/  
15 vinylbenzyl quaternary ammonium salt copolymer and a hydrophilic polymer selected from the group consisting of gelatin, poly(vinyl alcohol), and hydroxypropyl cellulose, and mixtures thereof. US-A-4 547 405 describes an ink jet recording sheet comprising a transparent support carrying a layer comprising a mixture of a coalesced block copolymer latex of poly(vinyl alcohol) with polyvinyl(benzyl  
20 ammonium chloride) and a water-soluble polymer selected from the group consisting of poly(vinyl alcohol), poly(vinylpyrrolidone) and copolymers thereof.

US-A-4 904 519 describes an ink jet recording sheet comprising a transparent polymeric backing having on at least one major surface thereof a transparent, ink-receptive layer comprising a cross-linked, hydrolyzed copolymer of  
25 a vinyl ester comonomer selected from the group consisting of vinyl acetate, vinyl propionate and vinyl stearate, and a vinyl amide comonomer selected from the group consisting of N-vinyl pyrrolidone and vinyl acetamide, the degree of hydrolysis being from about 80 to 95%, and the cross-linking being effected by an agent selected from the group consisting of borates, titanates, dichromates and aldehydes.

US-A-4 900 620 describes an ink jet recording sheet including a sheet-like substrate composed mainly of 70 to 100 wt % of wood pulp and 0 to 30 wt % of precipitated calcium carbonate and having a Stockigt sizing degree of not less than 2 seconds and not more than 25 seconds when formed into a sheet having a basis weight of 64 g/m<sup>2</sup>, and a coating layer composed mainly of white pigment, with the coating layer being formed on at least one side of the substrate at a weight of 1 to 10 g/m<sup>2</sup>. According to this patent, this sheet has a high ink absorption rate and is able to develop bright colors and sharp images.

US-A-5 139 867 describes transparent image-recording elements that contain ink-receptive layers that can be imaged by the application of liquid ink dots. The ink-receptive layers contain a combination of:

- (i) a vinyl pyrrolidone;
- (ii) particles of a polyester, namely a poly(cyclohexylenedimethylene-co-oxydiethylene isophthalate-co-sodio-sulfobenzenedicarboxylate);
- (iii) a homopolymer or a copolymer of an alkylene oxide containing from 2 to 6 carbon atoms;
- (iv) a polyvinyl alcohol;
- (v) a compound or a mixture of compounds having the general formula



wherein R<sub>1</sub> represents a hydrogen atom or a methyl group, R<sub>2</sub> and R<sub>3</sub> each represent a hydrogen atom, an alkyl group having a carbon number of 1 to 4 or a phenyl group, and n is an integer of 1 to 10; and

- (vi) inert particles.

US-A-4 592 954 describes a transparency for ink jet printing comprised of a supporting substrate and thereover a coating consisting essentially of a blend of carboxymethyl cellulose, and polyethylene oxides. Also disclosed are papers for use in ink jet printing comprised of a plain paper substrate and a coating thereover consisting essentially of polyethylene oxides.

US-A-5 342 688 describes an ink-receptive sheet comprising a transparent substrate bearing on at least major surface thereof an ink-receptive layer which comprises at least one imaging polymer and an effective amount of polymeric mordant, which comprises a polymethylene backbone carrying pendant aminoguanidino groups.

US-A-4 547 405 describes an ink jet recording sheet comprising a transparent support carrying a layer comprising a mixture of a coalesced block copolymer latex of poly(vinyl alcohol) with polyvinyl(benzyl ammonium chloride) and a water-soluble polymer selected from the group consisting of poly(vinyl alcohol), poly(vinylpyrrolidone) and copolymers thereof.

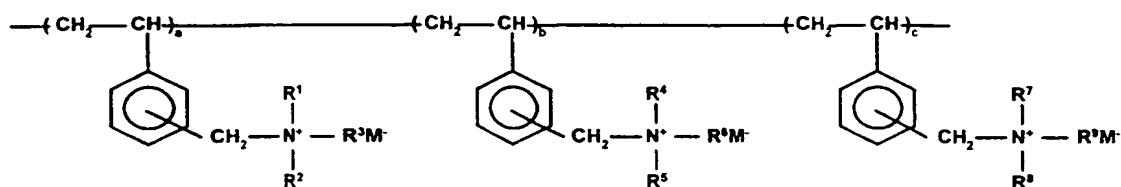
US-A-4 575 465 describes an ink jet recording sheet comprising a transparent support carrying a layer formed from a mixture of vinylpyridine/vinylbenzyl quaternary ammonium salt copolymer and a hydrophilic polymer selected from the group consisting of gelatin, poly(vinyl alcohol), and hydroxypropyl cellulose, and mixtures thereof.

It has now been found that the properties of ink jet recording sheets having ink-receiving layers which contain poly(vinyl alcohol) can be improved by using as the poly(vinyl alcohol) a mixture of derivatized and non-derivatized poly(vinyl alcohol). It has also been found that the properties of ink jet recording sheets having ink-receiving layers containing hydrophilic polymers can be improved by using, in the ink-receiving layer, a specific sub-group of vinylbenzyl quaternary ammonium salt copolymers and/or a poly(vinylpyridine). The ink jet recording sheets containing a poly(vinylpyridine) display improved imaging properties; in particular, the water fastness of the images produced on these sheets is substantially improved.

Accordingly, in one aspect this invention provides an ink jet recording sheet comprising a support carrying an ink-receiving layer, this ink-receiving layer comprising a non-derivatized poly(vinyl alcohol) and a derivatized

poly(vinyl alcohol). This form of the invention may hereinafter be called the "derivatized/non-derivatized sheet" of the invention.

In another aspect, this invention provides an ink jet recording sheet comprising a support carrying an ink-receiving layer, this ink-receiving layer comprising a hydrophilic polymer, and at least one of (a) a poly(vinylbenzyl quaternary ammonium salt) of the formula:



(wherein each of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  is independently alkyl of from 1 to 4 carbon atoms; each of  $R^7$ ,  $R^8$  and  $R^9$  is independently alkyl of from 1 to 18 carbon atoms and the total number of carbon atoms in  $R^7$ ,  $R^8$  and  $R^9$  is from 13 to 20; each  $M^-$  is an anion; and each of  $a$ ,  $b$  and  $c$  is the molar proportion of the respective repeating units) and (b) a poly(vinylpyridine). This form of the invention may hereinafter be called the "hydrophilic polymer sheet" of the invention.

The derivatized/non-derivatized sheet and the hydrophilic polymer sheet of the present invention are not mutually exclusive; as described in more detail below, useful sheets can be prepared using, for example, a mixture of derivatized and non-derivatized poly(vinyl alcohol) as the hydrophilic polymer, together with a poly(vinylbenzyl quaternary ammonium salt) and/or a poly(vinylpyridine).

This invention also provides a method of ink jet printing which comprises applying to an ink jet recording sheet a plurality of ink droplets generated from an ink jet printer, wherein the ink jet recording sheet is a sheet of the present invention.

The derivatized poly(vinyl alcohol) used in the derivatized/non-derivatized sheet of the present invention differs from conventional (also, for convenience referred to herein as "underivatized") poly(vinyl alcohol) in that at least some of the hydroxyl groups present in the underivatized poly(vinyl alcohol) are replaced by ether or ester groupings, preferably the latter. A preferred type of

derivatized poly(vinyl alcohol) for use in the present invention is an acetoacetylated poly(vinyl alcohol), in which the hydroxyl groups are esterified with acetoacetic acid. Acetoacetylated poly(vinyl alcohol) is available commercially, for example as Gohsefimer Z-200, sold by Nippon Gohsei, No. 9-6, Nozaki-cho, Kita-ku, Osaka, Japan. This material is stated by the manufacturer to be a super hydrolyzed poly(vinyl alcohol) having a degree of hydrolysis of 99-100%, a viscosity in 4% aqueous solution at 20°C of 13.3-14.3 cps and a pH in the same solution of 3.5-5.

A preferred underivatized poly(vinyl alcohol) for use in the derivatized/non-derivatized sheet is Airvol-205, sold by Air Products, Allentown, Pennsylvania, United States of America. This material is stated by the manufacturer to be a partially hydrolyzed poly(vinyl alcohol) having a degree of hydrolysis of 87-89%, a viscosity in 4% aqueous solution at 20°C of 5.2-6.2 cps and a pH in the same solution of 4.5-6.5.

It is important to use a mixture of derivatized and underivatized poly(vinyl alcohol) in the derivatized/non-derivatized sheet, since it has been found that the mixture has better ink absorbing characteristics than either component alone. Although the optimum mixture (which skilled persons can determine by routine empirical testing) will vary somewhat depending upon the particular derivatized and underivatized poly(vinyl alcohol)s used, in general it is preferred that the weight ratio of the non-derivatized poly(vinyl alcohol) to the derivatized poly(vinyl alcohol) in the ink-receiving layer be in the range of from about 2:1 to about 1:2; in some cases, uses of approximately equal weights of the two polymers gives the best results.

In addition to the derivatized and underivatized poly(vinyl alcohol)s, the ink-receiving layer of the derivatized/non-derivatized sheet also desirably comprises a mordant to improve the ink binding ability of the layer. Preferred mordants for this purpose are poly(vinylbenzyl quaternary ammonium salts), especially those of the formula given above. These mordants, and processes for their preparation, are described in US-A-4 794 067, which also claims image-receiving



elements containing these mordants. Preferably, the poly(vinylbenzyl quaternary ammonium salt) is one in which  $R^7$  is an alkyl group containing at least 11 carbon atoms, and  $R^8$  and  $R^9$  are each a methyl group. A specific preferred mordant of this type is that in which each of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^8$  and  $R^9$  is a methyl group; each of  $R^4$ ,  $R^5$  and  $R^6$  is an ethyl group; and  $R^7$  is an  $n\text{-C}_{12}\text{H}_{25}$  group; for convenience, this material is referred to in the Examples below simply as "Terpolymer". The molar proportions a, b and c are desirably in the ratios 5-10:5-10:1.

When the hydrophilic polymer sheets of the present invention contain a poly(vinylbenzyl quaternary ammonium salt), the preferred salts are the same as those preferred for use in the derivatized/non-derivatized sheets, as discussed in the preceding paragraph. When the hydrophilic polymer sheets of the present invention contain a poly(vinylpyridine), this polymer is very desirably a poly(4-vinylpyridine). It has been found that the properties of the ink-receiving layer are significantly affected by the process used to prepare the poly(4-vinylpyridine); desirably, the hydrophilic polymer used with poly(4-vinylpyridine) is poly(vinyl alcohol) and the poly(4-vinylpyridine) is prepared by polymerizing 4-vinylpyridine in the presence of at least part of the poly(vinyl alcohol). Such a polymerization may be conducted by the processes described in US-A-3 208 964 and US-A-3 507 846, but poly(4-vinylpyridine) produced by these two processes tends to produce some non-uniformity in black areas of images produced from the recording sheet. It is believed (although the invention is in no way limited by this belief) that this non-uniformity is due to the suspension polymerization mechanism of the processes described in these two patents, which may tend to cause certain heterogeneities in the product.

It has now been found that the uniformity of black areas of images produced on the present recording sheet is improved by effecting the polymerization of the 4-vinylpyridine using a precipitation polymerization procedure in which substantially all of the initiator, and most if not all of the 4-vinylpyridine, are present in solution. Accordingly, in a preferred procedure, the poly(4-vinylpyridine) used in the present recording sheet, is prepared by preparing an aqueous dispersion of

poly(vinyl alcohol) and contacting this aqueous solution with less than about 10 percent by weight (based upon the weight of the aqueous solution of 4-vinylpyridine monomer and a water-soluble free radical initiator. A preferred free radical initiator for use in this reaction is 2,2'-azobis(2-amidinopropane) hydrochloride, solid commercially by Wako Chemical, USA Inc., 1600 Bellwood Rd., Richmond, Virginia 23237, United States of America, under the Registered Trade Mark V50. By keeping the concentration of 4-vinylpyridine relatively low, the major part of this monomer is solubilized in the aqueous dispersion, allowing homogeneous initiation to occur and a more homogeneous product to be produced. This process has the further advantage that typically the residual monomer concentration in the product is greatly reduced, usually by about an order of magnitude, as compared with the products of the processes described in the two aforementioned patents.

As already noted, in this preferred polymerization process, at least part of the poly(vinyl alcohol) is present, and functions as an emulsifier and viscosity enhancer. It should be noted that in many cases it is not necessary to include in the polymerization reaction all of the poly(vinyl alcohol) which will eventually be admixed with the poly(4-vinylpyridine) in the ink-receiving layer. In particular, when the poly(4-vinylpyridine) in the ink-receiving layer is to comprise a mixture of a derivatized and an underivatized poly(vinyl alcohol) (i.e., when the sheet is to be both a derivatized/non-derivatized sheet and a hydrophilic polymer sheet of the present invention), it is often advantageous to include only the underivatized poly(vinyl alcohol) in the polymerization reaction and to add the derivatized poly(vinyl alcohol) later.

At the completion of the polymerization reaction, much of the poly(4-vinylpyridine) produced is in the form of a precipitate, and it is highly desirable to solubilize this polymer before the polymeric mixture is used to form the ink-receiving layer. To effect such solubilization, it is desirable to add an acid to the reaction product, a preferred acid for this purpose being lactic acid.

Although other hydrophilic polymers, for example gelatin or hydroxypropyl cellulose, may be used in the hydrophilic polymer sheets of the present invention, the preferred hydrophilic polymer in all such sheets is poly(vinyl alcohol), since this polymer has been found to give ink-receiving layers with the best ink-receiving properties. The optimum weight ratio of poly(vinyl alcohol) to total weight of poly(vinylbenzyl quaternary ammonium salt) and poly(vinylpyridine) for any particular ink may be determined by skilled persons using routine empirical tests; however, for general guidance it may be stated that typically from 3 to 15 parts, desirably from 5 to 8 parts, by weight of the poly(vinyl alcohol) per total part by weight of the poly(vinylbenzyl quaternary ammonium salt) and the poly(vinylpyridine) produces optimum results.

As already indicated, in the hydrophilic polymer sheets of the present invention containing poly(vinyl alcohol), this poly(vinyl alcohol) is desirably a mixture of derivatized and non-derivatized poly(vinyl alcohol), and desirably the weight ratio of the non-derivatized poly(vinyl alcohol) to the derivatized poly(vinyl alcohol) is in the range of 2:1 to 1:2, with the derivatized poly(vinyl alcohol) desirably being an acetoacetylated poly(vinyl alcohol).

In all ink jet receiving sheets of the present invention containing poly(vinyl alcohol), to produce an ink-receiving layer of optimum toughness and control of ink spreading, it is desirable that the poly(vinyl alcohol) be cross-linked. Such cross-linking may be effected with any of the known cross-linking agents for poly(vinyl alcohol), for example the boron compounds and chromium chloride described in the aforementioned US-A-4 592 951. However, in most cases it is preferred that the cross-linking agent be an aldehyde. However, in the case of hydrophilic polymer sheets containing poly(4-vinylpyridine), the preferred type of cross-linking agent is a diepoxy cross-linking agent; one preferred cross-linking agent of this type is 1,4-butanediol diglycidyl ether. Although such diepoxy cross-linking agents actually perform better under basic conditions, in practice in the present invention it may be desirable to include an acid, for example acetic acid or

lactic acid, to solubilize the poly(4-vinylpyridine) in the composition used to form the ink-receiving layer, and diepoxy cross-linking agents can still provide a satisfactory degree of cross-linking in the presence of such an acid. Whichever type of cross-linking agent is employed, it will typically be present in an amount of less than about 3 percent by weight of the ink-receiving layer.

In addition to the essential components already discussed, the ink-receiving layer of all the present sheets also advantageously comprises poly(vinyl pyrrolidone); this polymer acts to control ink reception by the ink-receiving layer and to control dot spread, i.e., the tendency for the ink droplets to spread laterally across the sheet. This polymer also improves the gloss of the sheet, producing a sheet with an appearance closely resembling that of conventional silver-halide based photographic printing paper. It is also advantageous to include starch granules (typically in an amount of from 2 to 8 percent by weight of the ink-receiving layer) in the ink-receiving layer in order that the feel of the sheet will closely resemble that of photographic printing paper. Finally, it has been found that including a surfactant in the ink-receiving layer further improves the ability of the layer to control dot spread; linear alkoxylated fatty alcohol surfactants, such as that sold commercially by BASF, Parsippany, New Jersey, United States of America, under the trade name Plurafac C17, are preferred for this purpose. Especially in the case of hydrophilic polymer sheets containing a poly(vinyl-pyridine), it may also be advantageous to include silica gel in the ink-receiving layer; such silica gel will typically be present in an amount of from 1 to 4 percent by weight of the ink-receiving layer. The inclusion of silica gel has been found to increase the smudge resistance of the image and also facilitates sheet handling during printing.

In preparing an ink jet recording sheet, it is necessary to consider not only the ink-receiving properties of the sheet, but also its mechanical properties. Most ink jet printers intended for home or small office use have an input tray for recording sheets at the front of the printer. Sheets withdrawn from this tray are carried 180° around a roller or roller assembly and thence across a platen, above

which one or more ink jet heads reciprocate to effect printing. The sheets are carried from the platen to an output tray positioned vertically above the input tray; typically, movable support members are provided on the output tray to hold a sheet emerging from the platen above the output tray for a few seconds, in order to prevent the sheet still "wet" from printing coming into contact with the preceding sheet and thus avoid smearing of the image on either sheet. Because of space constraints in the printer, the roller or roller assembly is usually only about 4 cm in diameter, and the recording sheet must be able to be wrapped around that small diameter without acquiring a permanent "set", so that the sheet will lie flat on the platen and in the output tray. It has been found advantageous to include a minor proportion of a poly(alkyl acrylate) or a poly(alkyl methacrylate) in the ink-receiving layer to improve the sheet feeding properties of the medium, poly(methyl methacrylate) being especially preferred for this purpose.

In addition to the components discussed above, the ink-receiving layer may comprise various conventional additives, for example ultraviolet absorbers, antioxidants, humectants, bactericides, fungicides and cross-linking agents.

The support employed in the present invention is not critical, and will normally be chosen having regard to the type of image which is intended to be produced, the proposed use of the image and the specific ink employed. The support may be transparent or opaque, depending upon whether a transparency or reflection print is desired. Polymeric films of both synthetic and naturally occurring polymeric materials may be employed. Examples of suitable transparent polymeric materials include polymethacrylic acid; methyl and ethyl esters; polyamides, such as nylons; polyesters, such as the polymeric films derived from ethylene glycol terephthalate acid; polymeric cellulose derivatives; polycarbonates; polystyrene and the like. Non-transparent supports include paper and synthetic papers such as silica-based synthetic papers. To promote adhesion of the ink-receiving layer to the support,

subcoats or surface treatments of the support, such as corona discharge, may be employed.

The ink jet recording sheet of the present invention is primarily intended for use with aqueous and alcohol based inks, although we do not exclude the possibility that the sheet may be useful in conjunction with inks based upon hydrophobic organic solvents such as hydrocarbons.

The ink jet recording sheet of the present invention can be prepared by conventional coating techniques. As illustrated in the Examples below, typically the various components of the ink-receiving layer will be prepared in the form of an aqueous solution or dispersion, coated on to the desired support and dried to produce the final recording sheet.

As already indicated, the proportions of the various components in the ink receiving layer may vary over a considerable range, but persons skilled in the art of preparing ink jet recording media will be able to determine the optimum proportions for any specific formulation by routine empirical tests. By way of general guidance, the following examples of preferred ranges of compositions of the ink-receiving layers in the present sheets are provided:

1. Derivatized/non-derivatized sheet:

from about 20 to about 40 parts by weight of a non-derivatized poly(vinyl alcohol);

from about 20 to about 40 parts by weight of an acetoacetylated poly(vinyl alcohol);

from about 5 to about 15 parts by weight of an a poly(vinylbenzyl quaternary ammonium salt);

from about 15 to about 30 parts by weight of poly(vinylpyrrolidone);

from 0 to about 5 (most desirably about 2) parts by weight of a poly(alkyl acrylate) or poly(alkyl methacrylate); and

from 0 to about 1 (most desirably about 0.2) part by weight of a surfactant;

2. Hydrophilic polymer sheet containing a poly(vinylbenzyl quaternary ammonium salt):

from about 50 to about 80 parts by weight of poly(vinyl alcohol);

from about 5 to about 15 parts by weight of the poly(vinylbenzyl quaternary ammonium salt);

from about 15 to about 30 parts by weight of poly(vinylpyrrolidone);

from 0 to about 5 (most desirably about 2) parts by weight of a poly(alkyl acrylate) or poly(alkyl methacrylate); and

from 0 to about 1 (most desirably about 0.2) part by weight of a surfactant; and

3. Hydrophilic polymer sheet containing a poly(vinylpyridine):

from about 50 to about 80 parts by weight of poly(vinyl alcohol);

from about 5 to about 15 parts by weight of poly(4-vinylpyridine);

from about 15 to about 30 parts by weight of poly(vinylpyrrolidone);

and

from 0 to about 1 (most desirably about 0.2) part by weight of a surfactant.

However, it will be appreciated that the optimum proportions of the various components in the ink-receiving layer of the present recording sheet may vary depending upon the chemical composition of the ink with which it is intended to be used, since such factors as ink spread, glossiness etc. are greatly affected by chemical interactions between the ink and the ink-receiving layer. Specifically, it has been found that, when the ink to be used for imaging contains a glycol ether cosolvent in addition to water, it is advantageous to increase significantly the proportion of poly(vinyl pyrrolidone) in the ink-receiving layer, up to as much as 80 percent of the layer, with consequent decreases in the proportion of the poly(vinyl alcohol) and the poly(vinyl pyridine). Accordingly, with such inks, the ink-receiving layer may comprises:

from about 10 to about 30 parts by weight of poly(vinyl alcohol)  
(which may be all derivatized poly(vinyl alcohol));

from about 5 to about 15 parts by weight of poly(4-vinylpyridine);

from about 50 to about 80 parts by weight of poly(vinyl pyrrolidone);

5 from 0 to about 5 parts by weight of silica gel;

from 0 to about 5 parts by weight of a cross-linking agent capable of  
cross-linking poly(vinyl alcohol) and poly(4-vinylpyridine); and

from 0 to about 1 part by weight of a surfactant.

10 The following Examples are now given, though by way of illustration  
only, to show particularly preferred reagents, conditions and techniques used in  
preparing the ink jet recording sheet of the present invention.

### Example 1

A dispersion was formed from the following components; all parts by  
weight are quoted on a dry solids basis:

15		<i>Parts by weight</i>
	Underivatized poly(vinyl alcohol) (Airvol 205)	33.0
	Acetoacetylated poly(vinyl alcohol) (Z200)	32.8
	Terpolymer	10.0
	Poly(vinyl pyrrolidone)	22.0
20	Poly(methyl methacrylate)	2.0
	Surfactant (Plurafac C17)	0.2

25 To prepare the dispersion, 115.5 grams of a 20 weight percent  
aqueous solution of Airvol 205, 287 grams of an 8 weight percent aqueous solution  
of Z200, and 55.6 grams of a 12.6 weight percent aqueous solution of terpolymer  
were added to 313 grams of water, and mixed in a air-driven mixer for 30 minutes.  
The surfactant (1.4 grams of a 10 weight percent aqueous solution), poly(methyl  
methacrylate) (35 grams of a 4 weight percent aqueous dispersion) and the  
poly(vinyl pyrrolidone) (192.5 grams of an 8 weight percent aqueous solution) were



then added, and the resultant mixture mixed for a further 30 minutes to produce a dispersion suitable for coating.

The dispersion thus produced was coated on to 7.6 mil polyclad photo paper using a No. 24 Mayer rod at a coating weight of 4.2 g/m<sup>2</sup>, and the coated sheets were dried at 80°C in an oven for 10 minutes. The dried ink jet recording sheets were tested using a Lexmark 2050 printer and were found to give excellent color images with minimal ink spread and smearing. Also, the printed sheets had a gloss and feel closely resembling that of conventional silver-halide based photographic printing paper. To test waterfastness, the printed images were placed into a beaker of deionized water for three minutes, taken out, shaken for 10 seconds and put back into water for another two minutes. The washed images showed very little dye fading. This is an indication of excellent waterfastness.

#### Example 2 (Control)

This Example illustrates that the excellent results achieved in Example 1 are not achieved using underivatized poly(vinyl alcohol) alone.

A dispersion was formed from the following components; all parts by weight are quoted on a dry solids basis:

	<i>Parts by weight</i>
Underivatized poly(vinyl alcohol) (Airvol 205)	65.8
Terpolymer	10.0
Poly(vinyl pyrrolidone)	22.0
Poly(methyl methacrylate)	2.0
Surfactant (Plurafac C17)	0.2

To prepare the dispersion, 230.3 grams of a 20 weight percent aqueous solution of Airvol 205 and 55.6 grams of a 12.6 weight percent aqueous solution of terpolymer were added to 485.2 grams of water, and mixed in a air-driven mixer for 30 minutes. The surfactant (1.4 grams of a 10 weight percent aqueous solution), poly(methyl methacrylate) (35 grams of a 4 weight percent aqueous dispersion) and the poly(vinyl pyrrolidone) (192.5 grams of an 8 weight

percent aqueous solution) were then added, and the resultant mixture mixed for a further 30 minutes to produce a dispersion suitable for coating.

The dispersion thus produced was coated, dried and the resultant sheet printed in the same way as in Example 1 above. The printed sheets were found to have a soft, tacky image in black areas.

### Example 3 (Control)

This Example illustrates that the excellent results achieved in Example 1 are not achieved using derivatized poly(vinyl alcohol) alone.

A dispersion was formed from the following components; all parts by weight are quoted on a dry solids basis:

	<i>Parts by weight</i>
Acetoacetylated poly(vinyl alcohol) (Z200)	65.8
Terpolymer	10.0
Poly(vinyl pyrrolidone)	22.0
Poly(methyl methacrylate)	2.0
Surfactant (Plurafac C17)	0.2

To prepare the dispersion, 575.75 grams of an 8 weight percent aqueous solution of Z200 and 55.6 grams of a 12.6 weight percent aqueous solution of terpolymer were added to 139.8 grams of water, and mixed in a air-driven mixer for 30 minutes. The surfactant (1.4 grams of a 10 weight percent aqueous solution), poly(methyl methacrylate) (35 grams of a 4 weight percent aqueous dispersion) and the poly(vinyl pyrrolidone) (192.5 grams of 8 weight percent aqueous solution) were then added, and the resultant mixture mixed for a further 30 minutes to produce a dispersion suitable for coating.

The dispersion thus produced was coated, dried and the resultant sheet printed in the same way as in Example 1 above. The printed sheets were found to have color images with slight ink smearing and pooling.

### Example 4 (Control)

This Example illustrates that the excellent results achieved in Example 1 are not achieved using a copolymer of vinylpyridine and a vinylbenzyl quaternary ammonium salt.

5                   Copolymer A used in the dispersion below was a copolymer of 4-vinylpyridine and vinylbenzyltrimethylammonium chloride, at a monomer ratio of 1:1.

A dispersion was formed from the following components; all parts by weight are quoted on a dry solids basis:

	<i>Parts by weight</i>
10           Underivatized poly(vinyl alcohol) (Airvol 205)	33.0
Acetoacetylated poly(vinyl alcohol) (Z200)	32.8
Copolymer A	10.0
Poly(vinyl pyrrolidone)	22.0
15          Poly(methyl methacrylate)	2.0
Surfactant (Plurafac C17)	0.2

20                   To prepare the dispersion, 231 grams of a 10 weight percent aqueous solution of Airvol 205, 287 grams of an 8 weight percent aqueous solution of Z200, and 70 grams of a 10.3 weight percent aqueous solution of Copolymer A were added to 185 grams of water, and mixed in a air-driven mixer for 30 minutes. The surfactant (1.4 grams of a 10 weight percent aqueous solution), poly(methyl methacrylate) (35 grams of a 4 weight percent aqueous dispersion) and the poly(vinyl pyrrolidone) (192.5 grams of an 8 weight percent aqueous solution) were then added, and the resultant mixture mixed for a further 30 minutes to produce a dispersion suitable for coating.

25

The dispersion thus produced was coated, dried and the resultant sheet printed in the same way as in Example 1 above. The printed sheets were found to have excellent color images with minimal ink spread and smearing. Also, the printed sheets had a gloss and feel closely resembling that of conventional silver-

halide based photographic printing paper. To test waterfastness, the printed images were placed into a beaker of deionized water for three minutes, taken out, shaken for 10 seconds and put back into water for another two minutes. The washed images showed approximately 30% dye fading, indicating poor waterfastness.

5

### Example 5 (Control)

This Example illustrates that the excellent results achieved in Example 1 are not achieved using a copolymer of vinylpyridine and a vinylbenzyl quaternary ammonium salt.

10 Copolymer B used in the dispersion below was a copolymer of 4-vinylpyridine and vinylbenzyltrimethylammonium chloride, at a monomer ratio of 3:1.

A dispersion was formed from the following components; all parts by weight are quoted on a dry solids basis:

		<i>Parts by weight</i>
15	Underivatized poly(vinyl alcohol) (Airvol 205)	33.0
	Acetoacetylated poly(vinyl alcohol) (Z200)	32.8
	Copolymer A	10.0
	Poly(vinyl pyrrolidone)	22.0
	Poly(methyl methacrylate)	2.0
20	Surfactant (Plurafac C17)	0.2

25 To prepare the dispersion, 231 grams of a 10 weight percent aqueous solution of Airvol 205, 287 grams of an 8 weight percent aqueous solution of Z200, and 77.6 grams of a 9.02 weight percent aqueous solution of Copolymer B were added to 185 grams of water, and mixed in a air-driven mixer for 30 minutes. The surfactant (1.4 grams of a 10 weight percent aqueous solution), poly(methyl methacrylate) (35 grams of a 4 weight percent aqueous dispersion) and the poly(vinyl pyrrolidone) (192.5 grams of an 8 weight percent aqueous solution) were then added, and the resultant mixture mixed for a further 30 minutes to produce a dispersion suitable for coating.

The dispersion thus produced was coated, dried and the resultant sheet printed in the same way as in Example 1 above. The printed sheets were found to have excellent color images with minimal ink spread and smearing. Also, the printed sheets had a gloss and feel closely resembling that of conventional silver-halide based photographic printing paper. To test waterfastness, the printed images were placed into a beaker of deionized water for three minutes, taken out, shaken for 10 seconds and put back into water for another two minutes. The washed images showed approximately 40% dye fading, indicating poor waterfastness.

#### Example 6 (Control)

This Example illustrates that the excellent results achieved in Example 1 are not achieved using a terpolymer of vinylpyridine, a vinylbenzyl quaternary ammonium salt and hydroxyethylcellulose.

Copolymer C used in the dispersion below was a terpolymer of 4-vinylpyridine, vinylbenzyltrimethylammonium chloride and hydroxyethyl-cellulose.

A dispersion was formed from the following components; all parts by weight are quoted on a dry solids basis:

#### *Parts by weight*

Underivatized poly(vinyl alcohol) (Airvol 205)	33.0
Acetoacetylated poly(vinyl alcohol) (Z200)	32.8
Copolymer C	10.0
Poly(vinyl pyrrolidone)	22.0
Poly(methyl methacrylate)	2.0
Surfactant (Plurafac C17)	0.2

To prepare the dispersion, 231 grams of a 10 weight percent aqueous solution of Airvol 205, 287 grams of an 8 weight percent aqueous solution of Z200, and 70 grams of a 10.3 weight percent aqueous solution of Copolymer C were added to 185 grams of water, and mixed in a air-driven mixer for 30 minutes. The surfactant (1.4 grams of a 10 weight percent aqueous solution), poly(methyl

methacrylate) (35 grams of a 4 weight percent aqueous dispersion) and the poly(vinyl pyrrolidone) (192.5 grams of an 8 weight percent aqueous solution) were then added, and the resultant mixture mixed for a further 30 minutes to produce a dispersion suitable for coating.

5           The dispersion thus produced was coated, dried and the resultant sheet printed in the same way as in Example 1 above. The printed sheets were found to have excellent color images with minimal ink spread and smearing. Also, the printed sheets had a gloss and feel closely resembling that of conventional silver-halide based photographic printing paper. To test waterfastness, the printed images  
10           were placed into a beaker of deionized water for three minutes, taken out, shaken for 10 seconds and put back into water for another two minutes. The washed images showed approximately 20% dye fading, indicating poor waterfastness.

#### Example 7

15           This Example illustrate a preferred process for the preparation of a mixed poly(vinyl alcohol)/poly(4-vinylpyridine) solution for use in a hydrophilic polymer sheet of the present invention.

310.6 kg of polyvinyl alcohol (Airvol 350, fully hydrolyzed) was solubilized in 5466 L of deaerated, deionized water at about 95°C under nitrogen for about forty-five (45) minutes, and then, cooled to about 65°C.

20           163.2 kg of 4-vinylpyridine monomer (Reilly Industries, Inc., 300 North Meridian Street, Suite 1600, Indianapolis, Indiana 46204, United States of America) and 75.6 L of deaerated, deionized water were added to the polyvinyl alcohol solution at about 65°C and stirred for about forty-five (45) minutes.

25           Next, 4.4 kg of water-soluble initiator (V50) in 37.8 L of deaerated, deionized water was added to the solution containing the poly(vinyl alcohol) and the 4-vinylpyridine monomer to initiate polymerization, which was allowed to proceed for about three (3) hours at about 65°C.

The weight average molecular weight of the poly(4-vinylpyridine) produced by the above polymerization process, determined by gel permeation chromatography (poly-2-vinylpyridine standard), is about 250,000.

5 The residual 4-vinylpyridine monomer concentration, determined by gas chromatography (10% polyethylene glycol, 2% potassium hydroxide, glass column, ¼ inch by 12 foot), is 97 parts per million (ppm).

To prepare the resultant fluid produced by the above process for use in coating an ink-receiving recording layer, the fluid was heated to about 90°C for thirty (30) minutes to destroy any remaining V50. After cooling the resultant fluid to  
10 about 60°C, 72.8 kg of 88% aqueous lactic acid and 1243 L of deionized water were added with stirring for thirty (30) minutes while maintaining the solution at about 60°C to solubilize the poly(4-vinylpyridine), and then, cooled to room temperature.

As will be appreciated from the data reported in this Example, no appreciable residual 4-vinylpyridine monomer remains in the resultant fluid of the  
15 polymerization process, i.e., less than 0.01% by weight, which is generally about a 10-fold reduction in resultant vinyl pyridine monomer when compared to the data reported in aforementioned US-A-3 507 846. It is thought that this reduction is due to a more homogeneous initiation derivable from the water solubility of the water-soluble initiator, and the amount of 4-vinyl pyridine monomer selected in the  
20 polymerization process of the present invention.

### Example 8

This Example illustrate a second preferred process for the preparation of a mixed poly(vinyl alcohol)/poly(4-vinylpyridine) solution for use in a hydrophilic polymer sheet of the present invention.

25 2.6 kg of poly(vinyl alcohol) (Airvol 540, partially hydrolyzed) was solubilized in 41 kg of deaerated, deionized water at about 95°C under nitrogen.

1.37 kg of 4-vinylpyridine monomer (Reilly Industries, Inc.) was added to the polyvinyl alcohol solution, and the temperature was increased to 65°C.

Next, 44 g of water-soluble initiator (V50) in 730 g of deaerated, deionized water was added to the solution containing the poly(vinyl alcohol) and the 4-vinylpyridine monomer to initiate polymerization, which was allowed to proceed for about three (3) hours at about 65°C.

5           The weight average molecular weight of the poly(4-vinylpyridine) produced by the above polymerization process, determined by gel permeation chromatography (poly-2-vinylpyridine standard), is about 215,000.

          The residual 4-vinylpyridine monomer concentration, determined by gas chromatography in the same way as in Example 7 above is 42 ppm.

10           To prepare the resultant fluid produced by the above process for use in coating an ink-receiving recording layer, the fluid was heated to about 90°C for thirty (30) minutes to destroy any remaining V50. After cooling the resultant fluid to about 60°C, 565 g of 88% aqueous acetic acid and 1 kg of deionized water were added with stirring for thirty (30) minutes while maintaining the solution at about  
15           60°C to solubilize the poly(4-vinylpyridine), and then, cooled to room temperature.

          As will be appreciated from the data reported in this Example, no appreciable residual 4-vinyl pyridine monomer remains in the resultant fluid of the polymerization process, i.e., less than 0.01% by weight.

### Example 9

20           This Example illustrates the preparation and printing of a hydrophilic polymer sheet of the present invention using the mixed polymer solution prepared in Example 7 above.

          A dispersion was formed from the following components; all parts by weight are quoted on a dry solids basis:



*Parts by weight*

	Underivatized poly(vinyl alcohol) (Airvol 350)	20.0*
	Poly(4-vinylpyridine)	10.0*
	Acetoacetylated poly(vinyl alcohol) (Z200)	39.0
5	Poly(vinyl pyrrolidone)	27.5
	Silica gel	2.0
	Diepoxy cross-linking agent	0.3
	Acetic acid	1.0
	Surfactant (Plurafac C17)	0.2

- 10     \*The underivatized poly(vinyl alcohol) and the poly(4-vinylpyridine) were added in the form of a mixed solution prepared as described in Example 7 above.

15             The mixed poly(vinyl alcohol)/poly(4-vinylpyridine) solution, and an aqueous solution of Z200, were added to water, and mixed in a air-driven mixer for 30 minutes. The surfactant, silica gel and poly(vinyl pyrrolidone) were then added, and the resultant mixture mixed for a further 30 minutes to produce a dispersion suitable for coating.

20             The dispersion thus produced was coated on to a 7.6 mil polyclad photo paper using a No. 24 Mayer rod at a coating weight of 4.2 g/m<sup>2</sup>, and the coated sheets were dried in a 80 °C oven for 10 minutes. The dried ink jet recording sheets were tested using a Hewlett Packard Deskjet (Registered Trade Mark) 693C printer and were found to give excellent color images with minimal ink spread and smearing. Also, the printed sheets had a gloss and feel closely resembling that of conventional silver-halide based photographic printing paper. To test waterfastness, cyan, magenta and yellow printed images were placed into a beaker of deionized water for three minutes, taken out, shaken for 10 seconds and put back into water for another two minutes. After the washed samples dried, color densities of cyan, magenta, and yellow were recorded using an X-Rite 310 photographic densitometer, supplied by X-Rite, Inc., Grandville, Michigan, United States of America, equipped

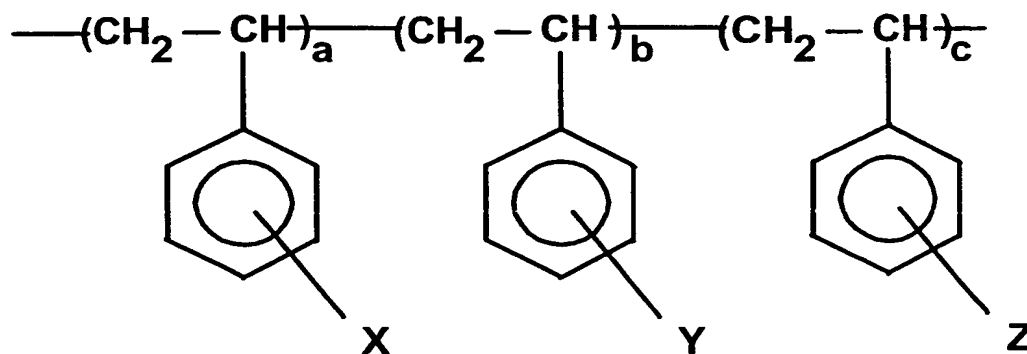
with the appropriate filter. The optical densities of the dry images before and after the immersion were as follows:

	<b>Cyan O.D.</b>	<b>Magenta O.D.</b>	<b>Yellow O.D.</b>
<b>Before immersion</b>	1.64	2.10	1.84
<b>After immersion</b>	1.52	2.09	1.08

These data indicate good waterfastness of the ink in the ink-receiving layer.

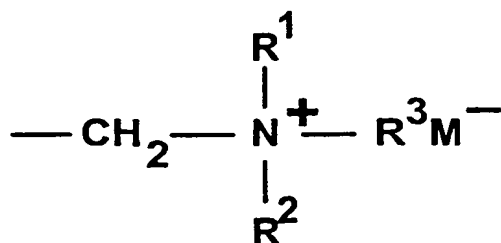
# CLAIMS

1. An ink jet recording sheet comprising a support carrying an ink-receiving layer, characterized in that the ink-receiving layer comprising a non-derivatized poly(vinyl alcohol) and a derivatized poly(vinyl alcohol).
2. An ink jet recording sheet according to claim 1 characterized in that the derivatized poly(vinyl alcohol) is an acetoacetylated poly(vinyl alcohol).
3. An ink jet recording sheet according to claim 1 or 2 characterized in that the weight ratio of the non-derivatized poly(vinyl alcohol) to the derivatized poly(vinyl alcohol) in the ink-receiving layer is in the range of from 2:1 to 1:2.
4. An ink jet recording sheet according to claim 1 characterized in that the ink-receiving layer further comprises a poly(vinylbenzyl quaternary ammonium salt).
5. An ink jet recording sheet comprising a support carrying an ink-receiving layer, this ink-receiving layer comprising a hydrophilic polymer, the recording sheet being characterized in that the ink-receiving layer further comprises at least one of (a) a poly(vinylbenzyl quaternary ammonium salt) of the formula:

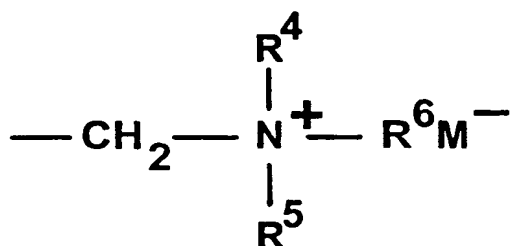


5

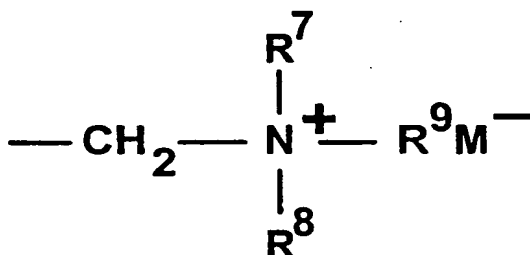
(wherein X is of the formula:



Y is of the formula:



Z is of the formula:



each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  is independently alkyl of from 1 to 4 carbon atoms; each of  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  is independently alkyl of from 1 to 18 carbon atoms and the total number of carbon atoms in  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  is from 13 to 20; each  $\text{M}^-$  is an anion; and each of a, b and c is the molar proportion of the respective repeating units) and (b) a poly(vinylpyridine):

6. An ink jet recording sheet according to claim 5 characterized in that the poly(vinylbenzyl quaternary ammonium salt) is one in which  $\text{R}^7$  is an

alkyl group containing at least 11 carbon atoms, and  $R^8$  and  $R^9$  are each a methyl group.

7. An ink jet recording sheet according to claim 6 characterized in that each of  $R^1$ ,  $R^2$  and  $R^3$  is a methyl group, each of  $R^4$ ,  $R^5$  and  $R^6$  is an ethyl group,  $R^7$  is a dodecyl group.

8. An ink jet recording sheet according to claim 5 characterized in that the poly(vinylbenzyl quaternary ammonium salt) is one in which the molar proportions a, b and c are in the ratios 5-10:5-10:1.

9. An ink jet recording sheet according to claim 6 characterized in that the poly(vinylpyridine) is a poly(4-vinylpyridine).

10. An ink jet recording sheet according to claim 9 characterized in that the hydrophilic polymer is poly(vinyl alcohol) and in that the poly(4-vinylpyridine) has been prepared by polymerizing 4-vinylpyridine in the presence of at least part of the poly(vinyl alcohol).

11. An ink jet recording sheet according to claim 10 characterized in that the poly(4-vinylpyridine) has been prepared by preparing an aqueous dispersion of poly(vinyl alcohol) and contacting this aqueous solution with less than 10 percent by weight (based upon the weight of the aqueous solution) of 4-vinylpyridine monomer and a water-soluble free radical initiator.

12. An ink jet recording sheet according to claim 11 characterized in that the free radical initiator comprises 2,2'-azobis(2-amidinopropane) hydrochloride.

13. An ink jet recording sheet according to claim 5 characterized in that the hydrophilic polymer is poly(vinyl alcohol).

14. An ink jet recording sheet according to claim 13 characterized in that the ink-receiving layer comprises from 3 to 15 parts by weight of the poly(vinyl alcohol) per total part by weight of the poly(vinylbenzyl quaternary ammonium salt) and the poly(vinylpyridine).

15. An ink jet recording sheet according to claim 14 characterized in that the ink-receiving layer comprises from 5 to 8 parts by weight of the poly(vinyl alcohol) per total part by weight of the poly(vinylbenzyl quaternary ammonium salt) and the poly(vinylpyridine).

16. An ink jet recording sheet according to claim 13 characterized in that the poly(vinyl alcohol) comprises a non-derivatized poly(vinyl alcohol) and a derivatized poly(vinyl alcohol).

17. An ink jet recording sheet according to claim 13 characterized in that the weight ratio of the non-derivatized poly(vinyl alcohol) to the derivatized poly(vinyl alcohol) being in the range of from 2:1 to 1:2.

18. An ink jet recording sheet according to claim 16 characterized in that the derivatized poly(vinyl alcohol) is an acetoacetylated poly(vinyl alcohol).

19. An ink jet recording sheet according to claim 13 characterized in that the poly(vinylpyridine) is a poly(4-vinylpyridine) and the poly(vinyl alcohol) and the poly(4-vinylpyridine) are cross-linked.

20. An ink jet recording sheet according to claim 19 characterized in that the poly(vinyl alcohol) and the poly(4-vinylpyridine) are cross-linked with a diepoxy cross-linking agent.

21. An ink jet recording sheet according to claim 1 or 13 characterized in that the poly(vinyl alcohol) is cross-linked.

22. An ink jet recording sheet according to claim 1 or 16 characterized in that the derivatized poly(vinyl alcohol) has been cross-linked with an aldehyde cross-linking agent.

23. An ink jet recording sheet according to claim 1 or 5 characterized in that the ink-receiving layer further comprises at least one of:

- (a) poly(vinylpyrrolidone);
- (b) a poly(alkyl acrylate) or a poly(alkyl methacrylate);
- (c) a surfactant; and
- (d) silica gel.

24. An ink jet recording sheet according to claim 23 characterized in that the surfactant is a linear alkoxylated fatty alcohol surfactant.

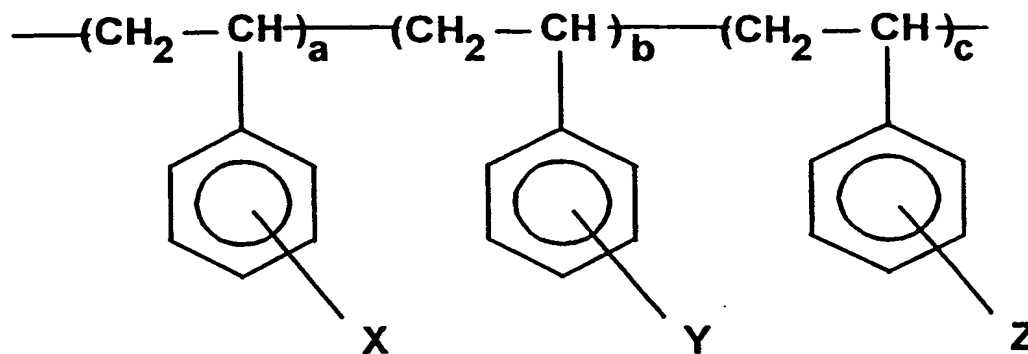
25. A method of ink jet printing which comprises applying to an ink jet recording sheet a plurality of ink droplets generated from an ink jet printer, the ink jet recording sheet comprising a support carrying an ink-receiving layer, characterized in that this ink-receiving layer is an ink-receiving layer according to claim 1 or 5.

5

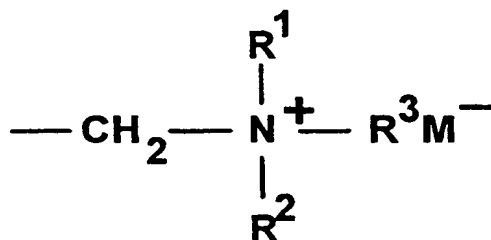
## AMENDED CLAIMS

[received by the International Bureau on 30 June 1998 (30.06.98);  
original claims 1-25 replaced by amended claims 1-24 (4 pages)]

1. An ink jet recording sheet comprising a support carrying an ink-receiving layer, characterized in that the ink-receiving layer comprising a non-derivatized poly(vinyl alcohol) and a derivatized poly(vinyl alcohol), the weight ratio of the non-derivatized poly(vinyl alcohol) to the derivatized poly(vinyl alcohol) being in the range of from 2:1 to 1:2.
2. An ink jet recording sheet according to claim 1 characterized in that the derivatized poly(vinyl alcohol) is an acetoacetylated poly(vinyl alcohol).
3. An ink jet recording sheet according to claim 1 characterized in that the ink-receiving layer further comprises a poly(vinylbenzyl quaternary ammonium salt).
4. An ink jet recording sheet comprising a support carrying an ink-receiving layer, this ink-receiving layer comprising a hydrophilic polymer, the recording sheet being characterized in that the ink-receiving layer further comprises at least one of (a) a poly(vinylbenzyl quaternary ammonium salt) of the formula:

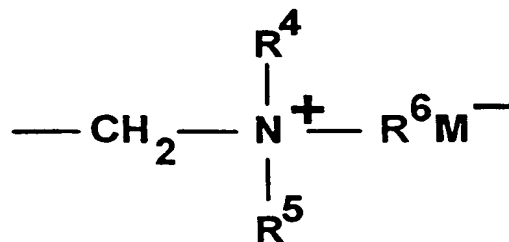


(wherein X is of the formula:

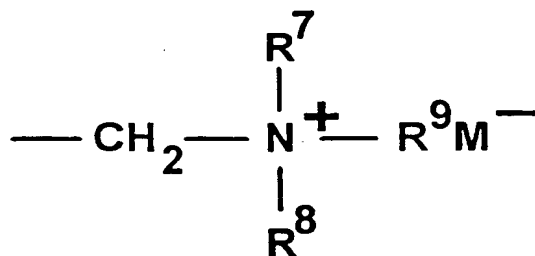




Y is of the formula:



10 Z is of the formula:



each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  is independently alkyl of from 1 to 4 carbon atoms; each of  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  is independently alkyl of from 1 to 18 carbon atoms and the total number of carbon atoms in  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  is from 13 to 20; each  $\text{M}^-$  is an anion; and each of a, b and c is the molar proportion of the respective repeating units) and (b) a poly(vinylpyridine).

5. An ink jet recording sheet according to claim 4 characterized in that the poly(vinylbenzyl quaternary ammonium salt) is one in which  $\text{R}^7$  is an alkyl group containing at least 11 carbon atoms, and  $\text{R}^8$  and  $\text{R}^9$  are each a methyl group.

6. An ink jet recording sheet according to claim 5 characterized in that each of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  is a methyl group, each of  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  is an ethyl group,  $\text{R}^7$  is a dodecyl group.

7. An ink jet recording sheet according to claim 4 characterized in that the poly(vinylbenzyl quaternary ammonium salt) is one in which the molar proportions a, b and c are in the ratios 5-10:5-10:1.

8. An ink jet recording sheet according to claim 4 characterized in that the poly(vinylpyridine) is a poly(4-vinylpyridine).

9. An ink jet recording sheet according to claim 8 characterized in that the hydrophilic polymer is poly(vinyl alcohol) and in that the poly(4-vinylpyridine) has been prepared by polymerizing 4-vinylpyridine in the presence of at least part of the poly(vinyl alcohol).

10. An ink jet recording sheet according to claim 9 characterized in that the poly(4-vinylpyridine) has been prepared by preparing an aqueous dispersion of poly(vinyl alcohol) and contacting this aqueous solution with less than 10 percent by weight (based upon the weight of the aqueous solution) of 4-vinylpyridine monomer and a water-soluble free radical initiator.

11. An ink jet recording sheet according to claim 10 characterized in that the free radical initiator comprises 2,2'-azobis(2-amidinopropane) hydrochloride.

12. An ink jet recording sheet according to claim 4 characterized in that the hydrophilic polymer is poly(vinyl alcohol).

13. An ink jet recording sheet according to claim 12 characterized in that the ink-receiving layer comprises from 3 to 15 parts by weight of the poly(vinyl alcohol) per total part by weight of the poly(vinylbenzyl quaternary ammonium salt) and the poly(vinylpyridine).

14. An ink jet recording sheet according to claim 13 characterized in that the ink-receiving layer comprises from 5 to 8 parts by weight of the poly(vinyl alcohol) per total part by weight of the poly(vinylbenzyl quaternary ammonium salt) and the poly(vinylpyridine).

15. An ink jet recording sheet according to claim 12 characterized in that the poly(vinyl alcohol) comprises a non-derivatized poly(vinyl alcohol) and a derivatized poly(vinyl alcohol).

16. An ink jet recording sheet according to claim 15 characterized in that the weight ratio of the non-derivatized poly(vinyl alcohol) to the derivatized poly(vinyl alcohol) being in the range of from 2:1 to 1:2.

17. An ink jet recording sheet according to claim 15 characterized in that the derivatized poly(vinyl alcohol) is an acetoacetylated poly(vinyl alcohol).

18. An ink jet recording sheet according to claim 12 characterized in that the poly(vinylpyridine) is a poly(4-vinylpyridine) and the poly(vinyl alcohol) and the poly(4-vinylpyridine) are cross-linked.

19. An ink jet recording sheet according to claim 18 characterized in that the poly(vinyl alcohol) and the poly(4-vinylpyridine) are cross-linked with a diepoxy cross-linking agent.

20. An ink jet recording sheet according to claim 1 or 12 characterized in that the poly(vinyl alcohol) is cross-linked.

21. An ink jet recording sheet according to claim 1 or 15 characterized in that the derivatized poly(vinyl alcohol) has been cross-linked with an aldehyde cross-linking agent.

22. An ink jet recording sheet according to claim 1 or 4 characterized in that the ink-receiving layer further comprises at least one of:

- (a) poly(vinylpyrrolidone);
- (b) a poly(alkyl acrylate) or a poly(alkyl methacrylate);
- (c) a surfactant; and
- (d) silica gel.

23. An ink jet recording sheet according to claim 22 characterized in that the surfactant is a linear alkoxylated fatty alcohol surfactant.

24. A method of ink jet printing which comprises applying to an ink jet recording sheet a plurality of ink droplets generated from an ink jet printer, the ink jet recording sheet comprising a support carrying an ink-receiving layer, characterized in that this ink-receiving layer is an ink-receiving layer according to claim 1 or 4.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/04117

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B41J 2/01; B41M 5/00

US CL : 347/105; 428/195, 500,520

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 347/105; 428/195, 500,520

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,478,631 A (KAWANO et al.) 26 December 1995, see col. 6; col. 8, lines 52-50.	1-25
Y	JP 57-182445 A (KOBAYASHI et al.) 10 November 1982, see entire abstract.	1-25

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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